Polymer Entanglement in Melts

Overlap Criterion:

need n chains in volume a^3: $n = \frac{a^3}{v_0 N_e}$

Kavassalis/Noolandi, Lin, Fetters

Dense Crowding/Packing

$G_e = \frac{kT}{v_0 N_e}$ $n = 20$ is universal (Fetters)

Polymer Entanglement in Solutions

Binary Contact Criterion:

Pairwise Interchain Contacts

Good Solvent same as overlap criterion because $a \sim \xi \sim \phi^{-3/4}$

$\Pi = \frac{kT}{\xi^3} \sim \phi^{9/4}$ $G_e = \frac{kT}{a^2 \xi} \sim \phi^{9/4}$

Θ Solvent

$\xi \sim \phi^{-1}$ measures ternary contacts

$\Pi = \frac{kT}{\xi^3} \sim \phi^3$

$a \sim \phi^{-2/3}$ measures binary contacts

$G_e = \frac{kT}{a^2 \xi} \sim \phi^{7/3}$

Polyelectrolyte Entanglement

Tube Diameter a

n entanglement strands in volume a^3

random walk of blobs $\frac{N_e}{g} \cong \left(\frac{a}{\xi}\right)^2$

$$a^3 \cong \xi^3 n \frac{N_e}{g}$$

$$n \cong \frac{a^3}{\xi^3}\frac{g}{N_e} \cong \frac{a}{\xi}$$

Simplest entanglement conjecture is constant n:

$$a \cong n\xi \sim c^{-1/2}$$

$$c_e \cong n^4 c^* \sim N^{-2}$$

Experimentally, $c_e \sim N^{-0.6}$, making $n \sim N^{0.35}$.

Scaling in Semidilute Solution

1. P. G. de Gennes, Scaling Concepts in Polymer Physics, Cornell Univ. Press (Ithaca, 1979).
2. P. G. de Gennes, P. Pincus, R. M. Velasco and F. Brochard, *J. Phys. (Paris)* **37**, 1461 (1976).
3. R. H. Colby, M. Rubinstein and M. Daoud, *J. Phys. II France* **4**, 1299 (1994).
4. M. Rubinstein, R. H. Colby and A. V. Dobrynin, *Phys. Rev. Lett.* **73**, 2776 (1994).
5. A. V. Dobrynin, R. H. Colby and M. Rubinstein, *Macromolecules* **28**, 1859 (1995).

Charged Polymer		Uncharged Polymer
$c^* \sim N^{-2}$	overlap concentration	$c^* \sim N^{-4/5}$
$c_e \cong 10^3\, c^*$	entanglement concentration	$c_e \equiv 10\, c^*$
$R \sim N^{1/2} c^{-1/4}$	coil size	$R \sim N^{1/2} c^{-1/8}$
	Unentangled ($c^* < c < c_e$)	
$\tau \sim N^2 c^{-1/2}$	relaxation time	$\tau \sim N^2 c^{1/4}$
$G = ckT/N$	terminal modulus	$G = ckT/N$
$\eta = G\tau \sim N\, c^{1/2}$	viscosity	$\eta = G\tau \sim N\, c^{5/4}$
$D = R^2/\tau \sim N^{-1} c^0$	diffusion coefficient	$D = R^2/\tau \sim N^{-1} c^{-1/2}$
	Entangled ($c > c_e$)	
$\tau \sim N^3 c^0$	relaxation time	$\tau \sim N^3 c^{3/2}$
$G = ckT/N_e \sim c^{3/2}$	terminal modulus	$G = ckT/N_e \sim c^{9/4}$
$\eta = G\tau \sim N^3 c^{3/2}$	viscosity	$\eta = G\tau \sim N^3 c^{15/4}$
$D = R^2/\tau \sim N^{-2} c^{-1/2}$	diffusion coefficient	$D = R^2/\tau \sim N^{-2} c^{-7/4}$

Dynamic viscoelasticity of dilute polyelectrolyte solutions

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J. Chem. Phys. **94** (6), 15 March 1991

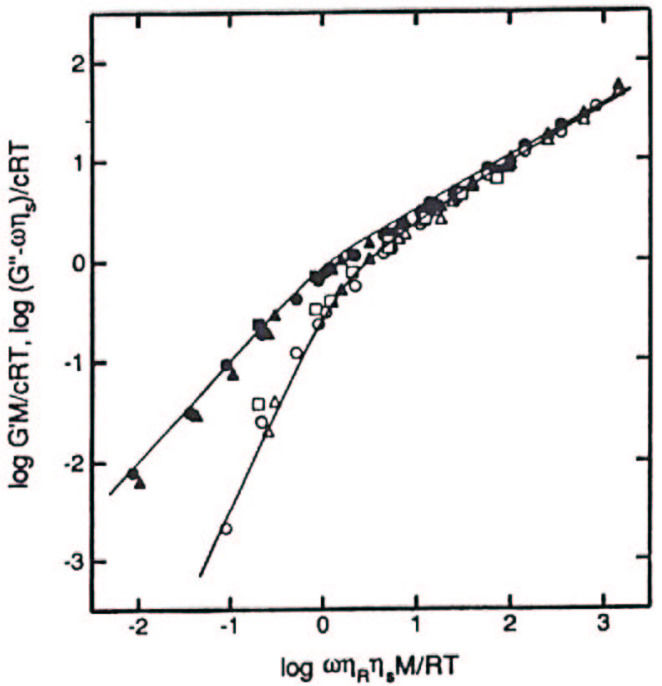
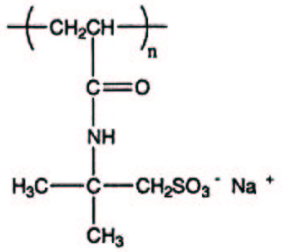


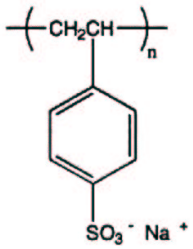
FIG. 7. The logarithmic plot of G'_R (open symbols) and G''_R (filled symbols) against $\omega\eta_s\eta_R M/RT$ for P2VP (3.0×10^4, 1.0×10^5, 2.4×10^5, and 1.0×10^6 MW) in 0.0023 M HCl at three concentrations (□ 0.5, △ 1.0, and ○ 2.0 mg mL^{-1}) of polymer. The curve is the Zimm bead-spring model with $h^* = 0.03$.

Poly(2-acrylamido-2-methylpropane sodium sulfonate)



NaPAMS

Sodium Poly(styrene sulfonate)



NaPSS

$c_e \sim N^{-0.6}$

c_e from η

c_e from D

c_e from χ

NaPSS

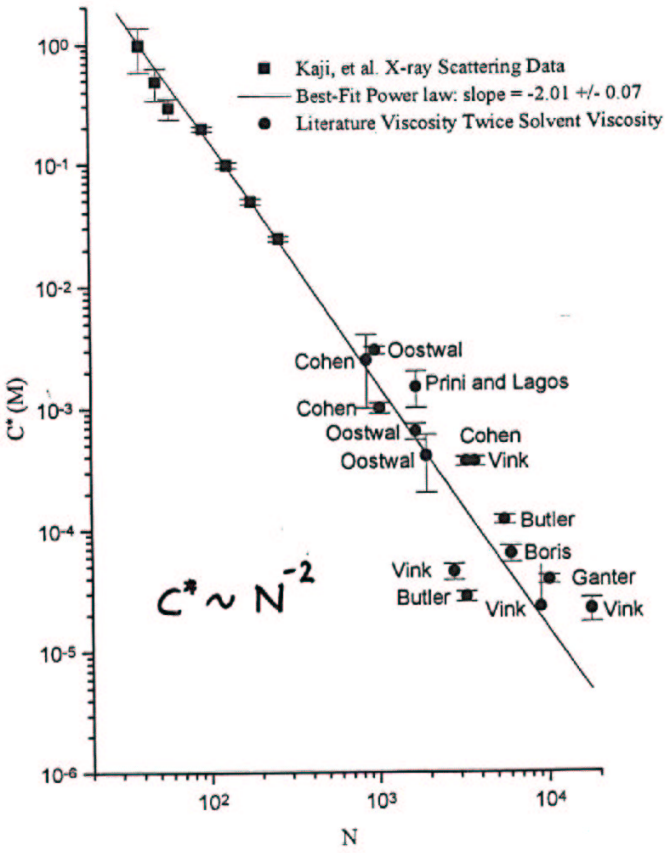
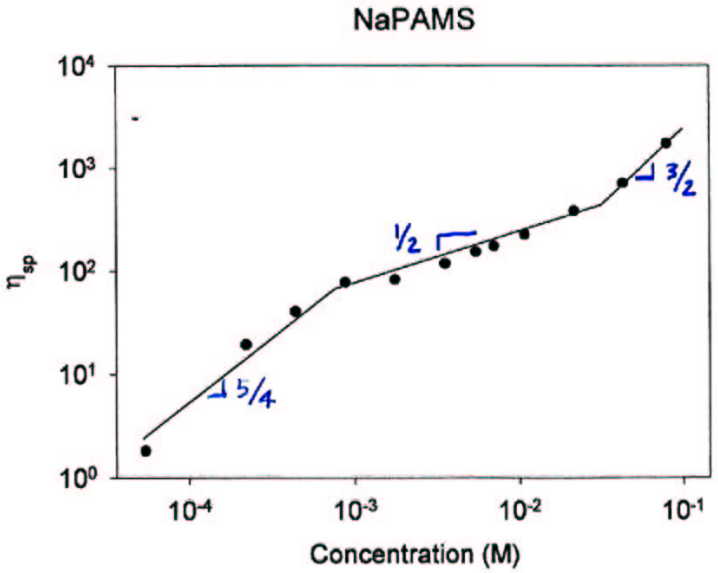
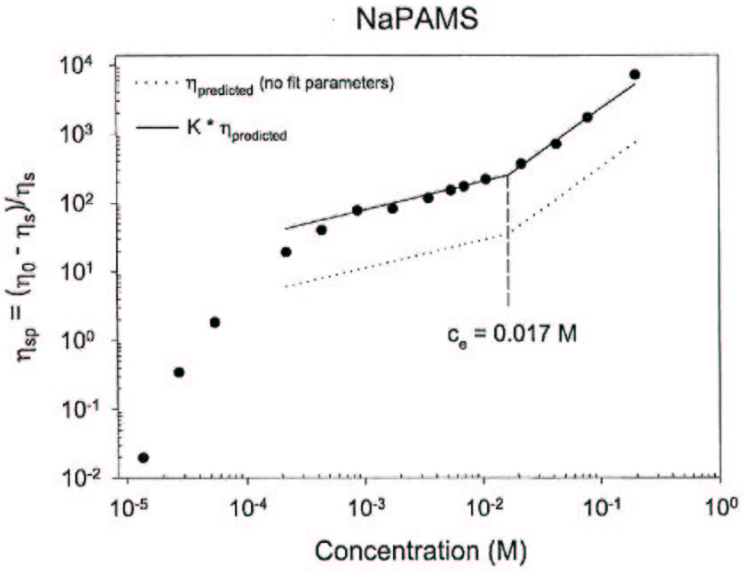


Figure 6.1 Plot of the dependence of the overlap concentration c^* upon degree of polymerization N extracted from various viscosity and scattering literature data.

Note: 1 ppm $\simeq 5 \times 10^{-6}$ M

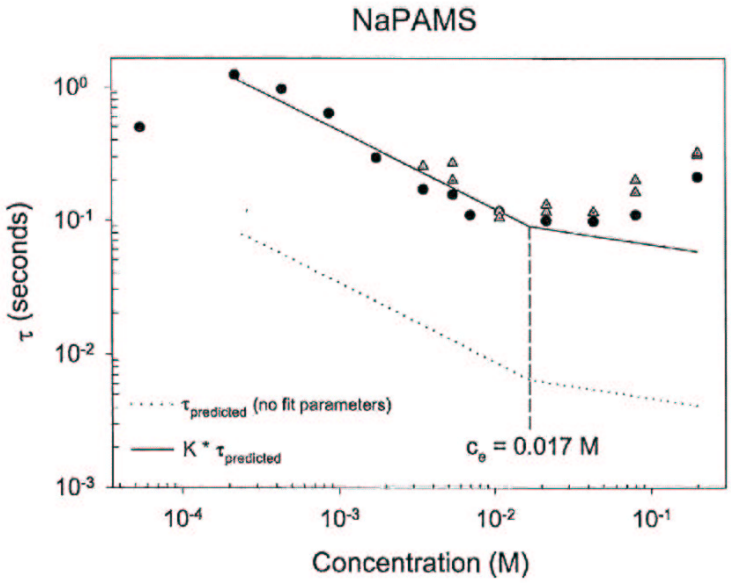
NaPAMS $M = 1.7 \times 10^6$ 100% sulfonated





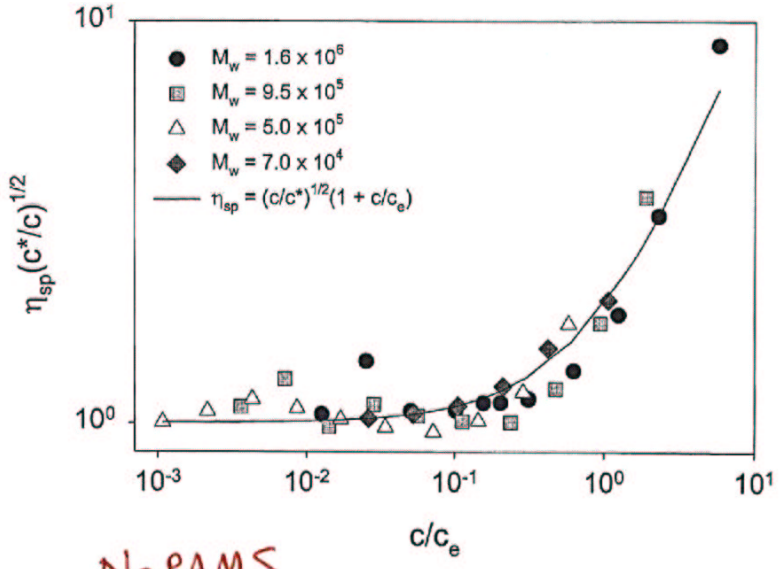
$$\eta_{sp} \sim \frac{N}{c R_g^3} \qquad c < c_e$$

$$\eta_{sp} \sim \frac{N}{c^3 R_g^9} \qquad c > c_e$$

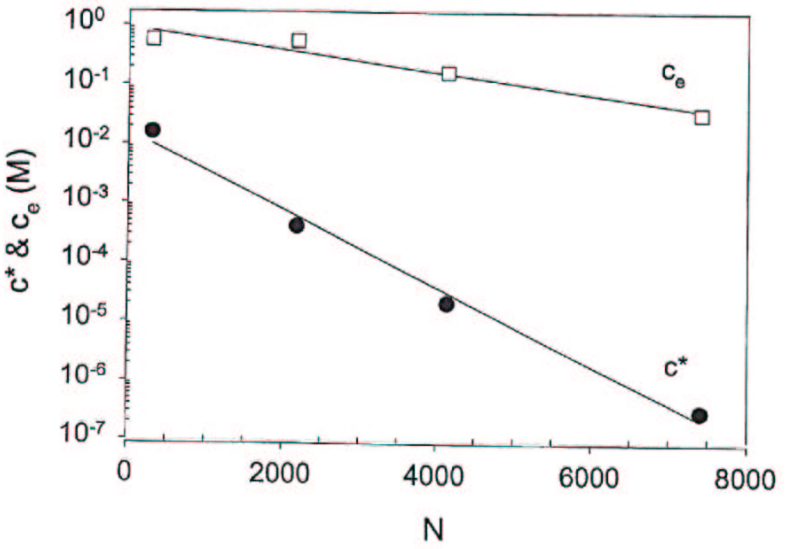


$$\tau \sim \frac{N^2}{c^2 R_g^3} \qquad c < c_e$$

$$\tau \sim \frac{N^3}{c^3 R_g^6} \qquad c > c_e$$

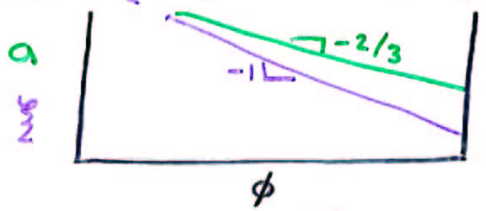


NaPAMS

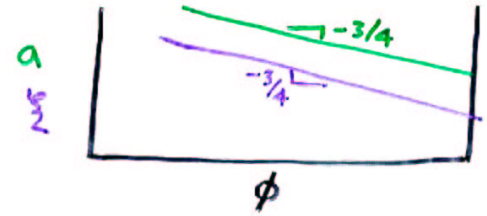


Length Scales in Solution

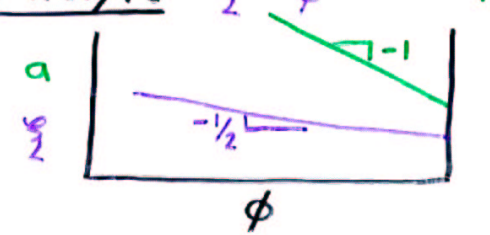
Θ Solvent $\xi \sim \phi^{-1}$ $a \sim \phi^{-2/3}$



Good Solvent $\xi \sim \phi^{-3/4}$ $a \sim \phi^{-3/4}$



Polyelectrolyte $\xi \sim \phi^{-1/2}$ $a \sim \phi^{-1}$



No theory for $a \sim \phi^{-1}$